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(54) Title: POLYMER BLENDS AND ARTICLES PRODUCED THEREWITH

(57) Abstract: A polymer blend comprising at least one acrylonitrile copolymer and at least one butadiene based polymer. The polymer blend may be formed into a variety of articles including gloves. The polymer blend exhibits increased softness and/or is free from latex allergens.

POLYMER BLENDS AND ARTICLES PRODUCED THEREWITH

FIELD OF THE INVENTION

The present invention relates to polymer blends of butadiene based
5 polymer(s) and acrylonitrile copolymer(s) and articles formed from the polymer
blends.

BACKGROUND OF THE INVENTION

Elastomeric articles such as gloves worn by surgeons and other
healthcare workers, condoms, and other sheath-like coverings have often been made
10 of materials such as natural rubber latex, a latex derived from the sap of the *Hevea*
Brasiliensis tree. Articles made from such natural rubber possess a number of
favorable qualities, including high intrinsic elasticity and effective protection as a
barrier from pathogens. Additionally, natural rubber is inexpensive and available in
large quantities. However, the use of natural rubber may cause problems to users
15 that are allergic to natural rubber latex proteins and allergens. Synthetic
alternatives to natural rubber protective sheath-like coverings to alleviate the risk of
allergenic reaction to the wearer have therefore been sought.

Various substitutes for natural rubber have been tried in the art.
Materials such as vinyl, nitrile, and synthetic butadiene rubber have individually
20 been used as substitutes for natural rubber, yet these materials typically suffer from
a number of disadvantages. For example, products such as gloves made from any
of the previously cited materials usually lack the distinctive feel and stretch of
natural rubber gloves, and thereby often fail to provide the sensitivity of touch
required by the wearer. Other sheath-like coverings suffer from similar problems.

Compounds such as vinyl and nitrile are typically both tough, and may tear easily and stretch poorly.

In addition to allergenic problems, synthetic materials used for sheath-like coverings-like products require not only adequate tensile strength and acceptable barrier property but also a particular tactile feel and comfort in order to be used to create articles such as gloves, finger cots, condoms, probe covers, etc. For such applications, synthetic polymer(s) or blends must feel "soft", i.e., must have a low modulus, so that sensation to the user's extremity that is covered by or in contact with the article created from the polymer or blend retains appropriate tactile sensation. Also, synthetic polymer(s) or blends should reduce hand fatigue for users, i.e., should have an acceptable level of residual stress exerted on the user hand by the sheath-like coverings due to stress relaxation.

Typically, conventional synthetic materials such as vinyl, nitrile, neoprene, or styrene butadiene rubber have been used for sheath-like coverings. However, such materials have often resulted in a sheath-like covering, particularly when used for surgical or examination gloves, that have a reduced tactile feel and/or stiffness.

A need remains for a synthetic polymer or polymeric blend that eliminates the risk of natural rubber latex allergic reaction when incorporated into a sheath-like covering. A further need remains to develop a polymer or polymeric blend with a sufficiently low modulus and residual stress that can be formed into a sheath-like covering that is soft and non-rigid so as to increase tactile sensation and reduce hand fatigue to the end user.

BRIEF SUMMARY OF THE INVENTION

The present invention relates to a polymeric blend that can be incorporated into a sheath-like covering that will not cause latex allergic reactions to the user of the covering. The invention further relates to a polymer blend having a low modulus and sufficient stress relaxation that can be used to produce a sheath-like covering having an increased tactile sensation.

The present invention relates to polymeric blends comprising at least one butadiene based polymer and at least one acrylonitrile copolymer. The polymer blend can be formed into various sheath-like coverings, particularly gloves for use by medical and industrial personnel.

5 Still further features and advantages of the invention will be apparent from the following detailed description when taken in conjunction with the appended claims.

DETAILED DESCRIPTION

The invention comprises a polymer blend, and elastomeric articles in
10 the shape of sheath-like coverings created from the polymer blend. Such elastomeric articles include gloves, condoms, finger cots, endoscope covers, ultrasound probe covers, and other similar sheath-like coverings. In one embodiment, the sheath-like coverings are industrial and medical gloves that are used for hand protection in the health care industry, scientific community, and other
15 critical environments. Such gloves include, but are not limited to, examination gloves, surgical gloves, procedure gloves, dental care gloves, clean room gloves, and laboratory gloves.

The polymer blend of the present invention comprises at least one butadiene based copolymer and at least one acrylonitrile copolymer. In one
20 embodiment, the polymer blend consists essentially of at least one butadiene based copolymer and at least one acrylonitrile copolymer, with no other polymers being present in the polymer blend. It has been surprisingly and unexpectedly discovered that this polymer blend may be used to produce an elastomeric article that has a low modulus, and therefore a soft feel. In one embodiment, the polymer blend of the
25 present invention has a modulus at 100% elongation of less than about 500 p.s.i. and/or modulus at 500% elongation of less than about 1500 p.s.i., and a percentage of stress retained at 100% elongation after 6 minutes of about 30% to about 80%. In another embodiment, the polymer blend has a modulus at 100% elongation of less than about 350 p.s.i. and/or modulus at 500% elongation of less than about

1000 p.s.i., and a percentage of stress retained at 100% elongation after 6 minutes of about 30% to 60%.

The acrylonitrile copolymer may be any acrylonitrile copolymer well known in the art, but in one embodiment is a copolymer of acrylonitrile and butadiene. The acrylonitrile copolymer may be carboxylated. The carboxylated acrylonitrile copolymer may be synthesized by copolymerization of acrylonitrile and butadiene with a small amount, typically less than 10%, of a monomer such as (meth)acrylic acid. The carboxylated acrylonitrile butadiene copolymer latex may also be purchased from various suppliers well known in the art, and may vary in the ratios of the three monomers used to synthesize the terpolymers.

The butadiene based polymer used in the blend may be any butadiene or its copolymers well known in the art. Examples of such butadiene based polymers include, but are not limited to, poly(2-chloro-1,3-butadiene) (commonly known as polychloroprene or neoprene) and its copolymers, poly(2-methyl-1,3-butadiene) (commonly known as polyisoprene) and its copolymers, polybutadiene and its copolymers, acrylonitrile-butadiene-styrene and its copolymers, and combinations thereof.

The butadiene based polymer and acrylonitrile copolymer may be blended in any amounts that yield a suitable product. In one embodiment, the polymer blend comprises 5 to 95 parts of one or more butadiene based polymers by weight and 95 to 5 parts acrylonitrile copolymer by weight, based on the total weight of the polymers. In another embodiment, the polymer blend comprises 10 to 90 parts of one or more butadiene based polymers by weight and 90 to 10 parts acrylonitrile copolymer by weight, based on the total weight of the polymers. In a further embodiment, the polymer blend comprises 75 to 50 parts or one or more butadiene based polymers by weight and 50 to 25 parts acrylonitrile copolymers by weight, based on the total weight of the polymers.

To further improve the softness, the polymer blend may also comprise one or more additional polymers such as natural rubber, chlorosulfonated polyethylene, chemically modified natural rubber, guayule rubber, butyl rubber, acrylic based rubber, polyurethane, fluoroelastomers, ethylene-propylene-diene

rubber (EPDM) or other diene based rubber and styrene diene based di- and tri-block copolymers. The additional polymers provide a more homogeneous blend dispersion and may also act as compatibilizer to the synthetic polymer blend. They are typically present in any required amounts, in one embodiment in amounts
5 ranging from about 5 to about 30 parts by weight, based on the total weight of the polymers.

All ranges recited herein include all combinations and subcombinations included within the range's limits; therefore, a range from "5% to 95%" would include ranges from 10% to 45%, from 30% to 47%, etc. A range of
10 "up to 800" would include ranges of up to 750, up to 625, etc. A range of "less than 1000" would include ranges of less than 800, less than 726, etc.

The polymer blend may include effective amounts of additional ingredients. These additional ingredients include crosslinking agents, vulcanization accelerators, vulcanization activator, antioxidants (also known as an antidegradant),
15 antiozonants, pigments, pH stabilizers, surfactants, emulsifying agents, fillers, softeners, defoamers, and combinations thereof. Preferably, these additional ingredients are added in the amounts by weight of the polymer blend as given below in Table 1:

Table 1

Ingredient	Proportion of Ingredient in parts per 100 by weight of the polymer blend
Polymer Blend	100
Crosslinker	0.05 to 5
Vulcanization Accelerator	0.10 to 10
Vulcanization Activator	0.10 to 10
Antioxidant	0.00 to 5
Antiozonant	0.00 to 5
Pigment	0.00 to 5
pH Stabilizer	0.05 to 5
Surfactant	0.00 to 5
Emulsifying Agent	0.01 to 5
Filler	0.00 to 10
Softener	0.00 to 20
Defoamer	0.00 to 2

It has been surprisingly and unexpectedly discovered that the addition of particular additives to the polymer blends will enhance the softness of sheath-like coverings produced therefrom. These include low molecular weight plasticizers such as mono-ester, diesters including adipates, azelates, benzoates, phthalates, sebacates, petroleum process oil, phosphate ester, and chlorinated paraffins. These additives need to be dispersed into a water based system before it can be added into a rubber blend latex. In one embodiment, the additive is a di-isodecylphthalate dispersion (Aquamix 916, Harwick Chemical Corporation, Ohio).

Typical crosslinkers include, but are not limited to, sulfur. Accelerators that promote the reaction between the crosslinkers such as sulfur and the polymers include, but are not limited to, amine derivatives, aldehyde-amine condensation products, thiazoles, dithiocarbamates, and guanidine derivatives. In one embodiment, the accelerator is zinc dibutylthiocarbamate. The accelerator may also comprise one or more metal oxide activators which include, but are not limited

to, zinc oxide. The antioxidant may comprise any such materials well known in the art, which include, but are not limited to, amine derivatives and/or phenol derivatives. The antiozonant may comprise any such materials well known in the art, which include, but are not limited to paraffinic waxes, microcrystalline waxes and intermediate types (which are blends of both paraffinic and microcrystalline waxes).

The polymer blend may also contain one or more pigments that are well known in the art. Such pigments typically include, but are not limited to, titanium dioxide, dyes, iron oxides and mixtures thereof. The polymer blend may also comprise one or more pH stabilizers that are well known in the art. The polymer blend may also comprise one or more emulsifying agents or reinforcing fillers or defoamers. Suitable emulsifying agents include non-ionic ethoxylated alkyl phenols such as octylphenoxy polyethoxyethanol or other non-ionic wetting agents. Defoamer may be chosen from naphthalene-type defoamers, silicone-type defoamers and other non-hydrocarbon-type defoamers. The polymer blend may also contain one or more softeners that include, but are not limited to, an ester, an adipate phthalate, silicate, stearate, phosphate, mineral oil or combinations thereof.

The polymer materials, including any optional additional ingredients, may be mixed together by any means known in the art, including, but not limited to, stirrer for latex mixing and Farrel Banbury or open-roll mills for dry rubber stocks blending. Optionally, one or more of the polymer materials in the polymeric blend may be mixed together with one or more optional ingredients to produce a compounded product. One or more further polymers may be added to this compounded product.

The polymer blend of the present invention may be used to produce sheath-like coverings by any standard methods known in the art. In one embodiment, formers in the shape of the object to be enclosed by the sheath-like coverings are used. The former may be in the shape of a glove, condom, endoscope probe, or other relevant shapes for which the sheath-like covering is to be used.

Typically, formers are cleaned by washing them with a detergent such as trisodium phosphate and/or a mild acid solution such as a citric acid

solution then rinsed in warm water. The clean formers are dried and then optionally may be heated to temperatures ranging from about 35°C to about 60°C. The formers are then typically dipped into an alcohol based or a water based coagulant dispersions. The coagulant dispersion may be heated, typically from 45°C
5 to about 60°C. The former is removed from the coagulant dispersion and may be allowed to air dry prior to being dipped into the compounded polymer blend latex. The former is then dipped into the compounded polymer blend latex. The compounded polymer blend latex is generally maintained at a temperature of about 20°C to about 30°C. The former is then removed from the compounded polymer
10 blend latex, with the sheath-like covering produced on the former. The former with the coagulated polymer blend latex may then be leached with water maintained at a temperature from about 30°C to about 60°C for a duration up to 7 minutes. The former may then be dipped into a powder slurry comprised of stabilizers, powders, and water. If required, a small amount of wetting agent, lubricant and biocide may
15 also be added. The powders generally used in the glove manufacturing are cross-linked corn starch powders and calcium carbonate powders. The former is then placed in an oven or other heat source and the sheath-like covering may be allowed to cure for up to 30 minutes at a temperature ranging up from about 100°C to 150°C. After curing, the former is cooled, typically to a temperature of about 45°C
20 or less. The sheath-like covering is then stripped from the former. For dry rubber stock, alternatives to this methodology well known in the art such as injection molding and other molding processes may also be used. It is understood that one of ordinary skill in the art will understand how to vary the times and temperatures of the process in accord with the article manufactured, the specific polymer blend
25 employed, particular formulation ingredients selected, and the manufacturing process used.

Coagulant dispersions are well known in the art; and typically include ingredients such as calcium carbonate, calcium nitrate, wetting agents, stabilizers, water (methanol for alcohol based coagulant dispersions). The

coagulant dispersion may also contain thickeners that include, but are not limited to, hydroxyethylcellulose, cellulosic based polymers and polyacrylates.

The sheath-like covering formed by the polymer blend of the present invention is substantially impermeable to water. It has a thickness appropriate such
5 that it is capable of being stretched to fit securely about the human body member or object to which it is formed to cover. Typically, the polymer blend is formed into a glove or preferably a surgical glove or examination glove. This glove will generally have a thickness from about 0.004 inches to about 0.015 inches.

The polymer blend of the present invention can be formed and cured
10 into a sheath-like covering having a low modulus, thereby having a "soft" feel for the end user. The degree of softness of an elastomeric article can generally be characterized by the modulus of the article at a specified elongation. In the case of glove manufacturing, the modulus at 100% and/or 500% elongation can be used to characterize the softness of the glove. Sheath-like coverings formed from the
15 polymer blends of the present invention have a low modulus, high elongation, high puncture resistance, high cut resistance, good ultra-violet resistance, good chemical resistance, good film rebound. The sheath-like coverings also have no latex protein and latex allergens.

Sheath-like coverings formed from the polymer blends of this
20 invention also exhibit greater oil and chemical resistance than those made from natural rubber latex, and better dexterity compared to those made from nitrile rubber alone.

In one embodiment, sheath-like coverings such as gloves made by the polymer blends of the present invention have a tensile strength of at least 1500
25 pounds per square inch (p.s.i.), a modulus at 100% elongation of less than 500 p.s.i., a modulus at 500% of less than about 1500 p.s.i., an elongation at break of at least about 500% and a percent residual stress at 100% elongation after 6 minutes of initial stretching of about 30% to about 80%.

Tensile strength, modulus properties and elongation at break are well
30 known in the art. Tensile strength is the energy required to stretch the film formed from the polymer blend to the breaking point. Elongation at break is the percent

stretch of the sheath-like covering formed from the polymer blend at the breaking point. The modulus at 500%, for example, is the energy required to stretch the sheath-like covering formed from the polymer blend to 500% of a predetermined length. The percentage of residual stress at 100% elongation after 6 minutes of
5 initial stretching is the percentage of the initial energy required to maintain a 100% stretching of the sheath-like covering after stretching for a period of 6 minutes.

The invention will be further described by reference to the following examples that are presented for the purpose of illustration only, and are not intended to limit the scope of the invention. Unless otherwise indicated, all parts are by
10 weight.

EXAMPLES

Example 1. Preparation of 100 Parts Neoprene Film.

Compounded neoprene was prepared as follows. The neoprene copolymer latex used in this example is a copolymer of neoprene and 2,3-dichloro-
15 1,3-butadiene which is available from DuPont Dow Elastomers (Louisville, Kentucky). The neoprene copolymer latex is anionic. The compounding agents used in compounding the neoprene copolymer latex are listed in Table 2.

Table 2

Ingredient	Proportion of Ingredient in parts per 100 by weight of the neoprene copolymer
Neoprene copolymer	100
Plasticizer stabilizer	0.5 to 5
Emulsifier stabilizer	0.5 to 5
Antiozonant	0.25 to 5
pH stabilizer sequestrate	0.10 to 1.5
PH stabilizer	0.10 to 1.5
Vulcanization activator	1 to 10
Crosslinker	0.5 to 3
Vulcanization accelerator	0.5 to 4
Antioxidant	0.1 to 3
White pigment	0.05 to 3
Yellow pigment	0.05 to 3
Rubber deodorant	0.001 to 1
Wetting agent	0.001 to 1
Defoamer	0.001 to 2

The compounding was done by first stirring the neoprene copolymer latex in a stainless steel tank. The stirring speed was adjusted to a level so that while the mixing was in effect, no air bubbles were created. The ingredients were filtered using a cheese cloth and then added to the neoprene copolymer latex according to the sequence listed in Table 2. Between each addition of a new ingredient, the neoprene copolymer latex was allowed to stir for at least 5 to 10 minutes. After compounding, the neoprene copolymer latex was matured at room temperature while stirring for at least 24 hours before the dipping was commenced.

Plates were then dipped into a water based coagulant dispersion maintained at about 55°C. The water based coagulant dispersion was comprised of 20% by weight of calcium nitrate (Aldrich, Milwaukee, Wisconsin), 0.3% by weight of hydroxyethylcellulose, 3% calcium carbonate, 0.3% by weight of acetylenic diol (Surfynol TG, Air Products & Chemicals, PA), and 76.4% by weight of soft water. After dipping, the plates were allowed to dry and then dipped

into the polymer blend latex, dwelled for about 30 seconds and removed. After that, the plates with the coagulated polymer blend latex were leached in water maintained at 35°C for few minutes. The plates were cured in an oven for 30 minutes at about 149°C. The formed film was removed and determined to have a uniform thickness of about 0.085 inches. The cured polymer blend films were then tensile tested on a tensile testing instrument (Model 5565, Instron Corporation, Canton, Massachusetts). Five samples were tested having a mean modulus at 500% of 241.2 p.s.i., a mean elongation of 1085%, and a mean tensile strength of 2943.7 p.s.i.

10

Example 2. Preparation of 90 Parts Neoprene/10 Parts Nitrile Polymer Blend Film

Ninety parts of compounded neoprene latex were blended with 10 parts of uncompounded nitrile latex. The neoprene was first compounded as taught in Example 1. The uncompounded nitrile latex is a carboxylated acrylonitrile butadiene terpolymer latex available from Synthomer Limited, United Kingdom (48C40, Batch 65565). No gelling or coagulation was observed upon mixing. The compounded neoprene and uncompounded acrylonitrile latexes were gently mixed using a stirrer. The stirring speed was adjusted to a level so as not to create air bubbles when the mixing action was in effect. The mixing was continued overnight before the dipping film was commenced.

The neoprene/acrylonitrile polymer blend was dipped on plates to form films as in Example 1. The films were removed from the plates and cut, and their thickness gauged. The films had a uniform thickness of about 0.008 inches. The cured polymer blend films were then tensile tested in the same manner as Example 1. Six samples were tested and found to have a mean modulus at 500% of 344.7 p.s.i., a mean elongation at break of 1007.2%, and a mean tensile strength of 3157.2 p.s.i.

30

Example 3. Preparation of 75 Parts Neoprene/25 Parts Nitrile Polymer Blend Film

Seventy-five parts of the compounded neoprene latex was added to 25 parts of uncompounded nitrile latex as taught in Example 2. The neoprene latex
5 was first compounded as taught in Example 1.

The neoprene/acrylonitrile polymer blend was dipped on plates to form films as in Example 1. The formed film was removed and determined to have a uniform thickness of about 0.009 inches. Five samples were tested having a mean modulus at 500% of 613.5 p.s.i., a mean elongation of 826.9%, and a mean tensile
10 strength of 3498.7 p.s.i.

Example 4. Preparation of 50 Parts Neoprene/50 Parts Nitrile Polymer Blend Film

Fifty parts of the compounded neoprene latex was added to 50 parts
15 of uncompounded nitrile latex as taught in Example 2. The neoprene latex was first compounded as taught in Example 1.

The neoprene/acrylonitrile polymer blend was dipped on plates to form films as in Example 1 except that the dwell time in the latex was 15 seconds. The formed film was removed and determined to have a uniform thickness of about
20 0.0079 inches. Five samples were tested having a mean modulus at 500% of 265.5 p.s.i., a mean elongation of 919.9%, and a mean tensile strength of 1629.8 p.s.i.

Example 5. Preparation of 100 Parts Nitrile Film

Compounded nitrile latex was prepared as follows. The nitrile latex
25 used in this example was a terpolymer of carboxylated acrylonitrile butadiene available from Synthomer Limited, United Kingdom (Grade 48C40, Batch 65565). The compounding agents used in compounding the nitrile latex are listed in Table 3.

The stabilizer used in a nonsodium salt of sulfated methyl oleate (Darvan SMO, R.T. Vanderbilt, CT).

Table 3

Ingredient	Proportion of Ingredient in parts per 100 by weight of the nitrile polymer
Nitrile polymer	100
Stabilizer	1.0 to 3.0
Zinc oxide	0.4 to 0.6
Sulfur	0.4 to 0.6
Zinc dibutylthiocarbamate	0.2 to 0.4
Potassium hydroxide	1.0 to 2.0

5

The compounding was done by first stirring the nitrile latex in a stainless steel tank. The stirring speed was adjusted to a level that the mixing was in effect and no air bubbles were created. The ingredients were filtered using a cheese cloth and then added to the nitrile latex according to the sequence listed in Table 3. Between each addition of a new ingredient, the nitrile latex was allowed to stir for at least 5 to 10 minutes. After compounding, the nitrile latex was matured at room temperature while stirring for at least 24 hours before the dipping was commenced.

The nitrile polymer was dipped on plates to form films as in Example 1 except that the curing temperature in the oven was maintained at 110°C. The films were removed from the plates and cut, and their thickness gauged. The films had a uniform thickness of about 0.0067 inches. The cured polymer blend films were then tensile tested in the same manner as Example 1. Four samples were tested and found to have a mean modulus at 500% of 928.3 p.s.i., a mean elongation at break of 699.9%, and a mean tensile strength of 4129.8 p.s.i.

20

Example 6. Preparation of 10 Parts Neoprene/90 Parts Nitrile Polymer Blend Film

Ninety parts of compounded nitrile latex were blended with 10 parts of uncompounded neoprene latex. The nitrile latex was first compounded as taught in Example 5. The uncompounded neoprene is a copolymer latex of 2-chloro-1,3-butadiene and 2,3-dichloro-1,3-butadiene available from DuPont Dow Elastomers (Louisville, Kentucky). The compounded nitrile and uncompounded neoprene latexes were gently mixed using a stirrer. The stirring speed was adjusted to a level so as not to create air bubbles while the mixing action was in effect. The mixing was continued overnight before the dipping film was commenced.

The neoprene/nitrile polymer blend was dipped on plates to form films as in Example 5. The films were removed from the plates and cut, and their thickness gauged. The films had a uniform thickness of about 0.0068 inches. The cured polymer blend films were then tensile tested in the same manner as Example 1. Three samples were tested and found to have a mean modulus at 500% of 542.1 p.s.i., a mean elongation at break of 755.9%, and a mean tensile strength of 2564.8 p.s.i.

Another batch of neoprene/nitrile polymer blend films was also prepared as taught in Example 5 except that the films were cured at 149°C. The films had a uniform thickness of about 0.007 inches. Three samples were tested and found to have a mean modulus at 500% of 604 p.s.i., a mean elongation at break of 768.7%, and a mean tensile strength of 3290.7 p.s.i.

Example 7. Preparation of 20 Parts Neoprene/80 Parts Nitrile Polymer Blend Film

Eighty parts of the compounded nitrile latex was blended with 20 parts of uncompounded nitrile latex as taught in Example 6. The nitrile latex was first compounded as taught in Example 6.

The neoprene/nitrile polymer blend was dipped on plates to form films as in Example 5. The films were removed from the plates and cut, and their thickness gauged. The films had a uniform thickness of about 0.0072 inches. The

cured polymer blend films were then tensile tested in the same manner as Example 1. Four samples were tested and found to have a mean modulus at 500% of 411.8 p.s.i., a mean elongation at break of 784.1%, and a mean tensile strength of 2211.7 p.s.i.

5 Another batch of neoprene/nitrile polymer blend films was also prepared as taught in Example 5 except that the films were cured at 149°C. The films had a uniform thickness of about 0.0074 inches. Two samples were tested and found to have a mean modulus at 500% of 439.4 p.s.i., a mean elongation at break of 852.6%, and a mean tensile strength of 3206.4 p.s.i.

10

Example 8. Preparation of 30 Parts Neoprene/70 Parts Nitrile Polymer Blend Film

Seventy parts of the compounded nitrile latex was blended with 30 parts of uncompounded neoprene latex as taught in Example 6. The nitrile latex
15 was first compounded as taught in Example 6.

The neoprene/nitrile polymer blend was dipped on plates to form films as in Example 5. The films were removed from the plates and cut, and their thickness gauged. The films had a uniform thickness of about 0.0077 inches. The cured polymer blend films were then tensile tested in the same manner as Example
20 1. Four samples were tested and found to have a mean modulus at 500% of 561.1 p.s.i., a mean elongation at break of 647.5%, and a mean tensile strength of 1337.6 p.s.i.

Another batch of neoprene/nitrile polymer blend films was also prepared as taught in Example 5 except that the films were cured at 149°C. The
25 films had a uniform thickness of about 0.0074 inches. Two samples were tested and found to have a mean modulus at 500% of 603.4 p.s.i., a mean elongation at break of 686%, and a mean tensile strength of 1957.4 p.s.i.

Example 9. Preparation of 70 Parts Nitrile/20 Parts Neoprene/10 Parts Polybutadiene Polymer Blend Film

70 milliliters (ml) of compounded carboxylated NBR latex were mixed with 20 ml of neoprene copolymer latex (Neoprene 750, DuPont Dow Elastomers, Louisville, Kentucky) and 10 ml of polybutadiene (Tylac 97924, Lot # 2012944, Reichhold Chemicals, Research Triangle Park, North Carolina.). The compounded nitrile latex was prepared as taught in Example 5 except for the following formulation change. The nitrile latex used in this example is a terpolymer of carboxylated acrylonitrile butadiene available from Reichhold Chemicals, Research Triangle Park, North Carolina (Tylac 68077). The nitrile latex was compounded with 100 parts of Tylac 68077, 0.75 part of zinc oxide, 1.0 part of sulfur, 0.3 part of zinc dibutylthiocarbamate, 0.5 part of Wingstay L and 1.25 part of titanium dioxide. The pH of the blend latex was adjusted to pH 9.2 and the total solid content of the blend latex was adjusted to 44% using soft water.

A glove former was preheated in an oven maintained at 57°C for about 1 minute and 15 seconds. The former temperature at the time of dipping was about 37°C. The former was dipped in a water based coagulant dispersion maintained at a temperature of about 49°C for about 10 seconds. The water based coagulant dispersion was comprised of 22.5% by weight of calcium nitrate, 7.7% by weight of calcium carbonate, 0.1% by weight of acetylenic diol (Surfynol TG, Air Products & Chemicals, PA), and 69.6% by weight of soft water.

The former was removed from the coagulant dispersion and was allowed to dry at about 25°C for about 30 seconds. The former was then dipped into the compounded polymer blend latex for about 20 to 30 seconds, with the polymer blend latex maintained at a temperature of about 25°C. The former with the coagulated blend latex was leached in water at about 18°C for about 4.5 minutes. The leached latex film was then dipped into a powder slurry dispersion at a temperature of about 26°C. The powder slurry dispersion was comprised of 0.9 lbs of stabilizer #725 (General Latex & Chemicals, Ohio), 6.8 lbs of stabilizer #727 (General Latex & Chemicals, Ohio), 40 lbs. of corn starch (Keo-Flo, The

Huubinger Company, Ohio), 670 mls of sodium hypochlorite, 4 lbs. of silicone emulsion (SM2140, General Electric, New York) and 655 lbs. of soft water.

The coagulated blend film was cured in an oven at a temperature of about 149°C for about 14 to 20 minutes. The blend film had a uniform thickness of about 0.009 inches and had a softer feel than films made from 100 parts of nitrile latex. The blend film had a tensile strength of 1732 p.s.i., a modulus at 100% elongation of 206 p.s.i., a modulus at 500% of 776 p.s.i., and an elongation of 631%.

10 **Example 10. Preparation of 70 Parts Nitrile/20 Parts Neoprene/10 Parts Chlorosulfonated Polyethylene Polymer Blend Film**

70 ml of compounded nitrile latex was mixed with 20 ml neoprene copolymer latex and 10 ml of chlorosulfonated polyethylene latex (Chemlok HYP-605, Lord Chemical product, Eric/PA) as taught in Example 9. The blend film was prepared as taught in Example 9. The blend film had a uniform thickness of about 0.01 inches and had a softer feel than films made from 100% parts of nitrile latex.

Example 11. Preparation of 80 Parts Nitrile / 20 Parts Polybutadiene Polymer Blend Film

20 80 ml of compounded nitrile latex was mixed with 20 ml of polybutadiene latex as taught in Example 9. The blend film was prepared as taught in Example 9. The blend film had a uniform thickness of about 0.011 inches and had a softer feel than films made from 100% parts of nitrile latex. The blend film had a 40% stress retained at 100% elongation after 6 minutes of stretching.

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Example 12. Preparation of 80 Parts Nitrile/20 Parts Acrylonitrile-Butadiene-Styrene Copolymer Blend Film.

80 ml of compounded nitrile latex was mixed with 20 ml of acrylonitrile-butadiene-styrene copolymer latex (Hycar 1570X75, B.F. Goodrich Chemical Co., AB 70136, Cleveland, Ohio). A finger cot was made by dipping the appropriate shaped former in the latex as described in Example 9. The blend film

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felt more rigid than the films made in Examples 10 and 11, however, it felt softer than the films made from 100% parts of nitrile latex.

Example 13. Preparation of 75 Parts Nitrile/20 Parts Enzyme Treated Natural Rubber/5 Parts Neoprene Polymer Blend Film

Seventy-five parts of nitrile (Tylac 68077, Reichold Chemicals, Research Triangle Park, North Carolina, Lot # 2012944), 20 parts of enzyme treated natural rubber and 5 parts of neoprene copolymer latex were mixed and compounded with additional ingredients as described in Table 4. The compounds were added in the order listed and potassium hydroxide (Aldrich, Milwaukee, Wisconsin) was added to bring the pH to 9.75.

Table 4

Compound	Parts	Total Solids Content (TSC), %	Dry Wt. g	Wet Wt. g
Tylac 68077	75.0	43.4	1173.2	2703.3
Natural Rubber	25.0	56.1	391.1	697.1
Neoprene 750	5.00	50.4	78.27	155.3
Darvan WAQ	1.005	33.2	15.73	47.37
Potassium Hydroxide	0.897	10.0	37.895	140.35
Sulfur	1.01	60.1	15.794	26.279
Zinc Oxide	0.750	71.2	11.73	16.48
ZDBC	0.300	54.8	4.690	8.558
TiO ₂	1.25	57.6	19.6	34.024
Wingstay L	0.504	43.9	7.889	17.97

The vulcanization activator, zinc oxide and antioxidant, Wingstay L were supplied by Akron Dispersions, Akron, Ohio. The stabilizer used was sodium lauryl sulfate (Darvan WAQ) supplied by R. T. Vanderbilt, CT. ZDBC (zinc dibutylthiocarbamate, vulcanization accelerator), sulfur (crosslinker) and titanium

dioxide (pigment) were all supplied by Allegiance Healthcare Penang, Malaysia. The latex blend was filtered and allowed to stir for approximately 3 hours before use. The blend was formed into gloves as taught in Example 9.

Tensile testing was performed and the results are given below in Table

5 5.

Table 5

	Thickness (in)	Tensile strength (psi)	Elongati on (%)	Modulus @ 100% Elongatio n (psi)	Modulus @300% Elongatio n (psi)	Modulus @400% Elongatio n (psi)	Modulus @500% Elongatio n (psi)	Modulus @600% Elongatio n (psi)
Sample 1	0.0048	2169	547	211	493	792	1477	—
Sample 2	0.0047	2181	601	188	431	652	1094	2163
Sample 3	0.0056	2333	541	196	486	807	1618	—
Sample 4	0.0051	2450	620	208	466	679	1070	209
Sample 5	0.0050	2359	593	212	484	730	1218	1169
Mean	0.0050	2298	580	203	472	732	1295	0
SD	3.51E-4	121	35	11	25	68	242	0
Median	0.0050	2333	593	208	484	730	1218	0
Mean + 2.00 SD	0.0057	2540	650	224	522	868	1780	0
Mean - 2.00 SD	0.0043	2057	511	182	422	596	811	0

Example 14. Preparation of 75 Parts Nitrile/5 Parts Neoprene/ 20 Parts

10 **Polyisoprene Blend Film.**

A nitrile/neoprene/polyisoprene latex blend was prepared as follows. 4581.3 grams of nitrile latex was placed in a stainless steel tank. The following components listed in Table 6 were then slowly added in the order listed.

Table 6

Compound	Parts	TSC %	Dry Wt. g	Wet Wt. g
Darvan WAQ	1.00	33.20	26.510	79.85
Neoprene 750	5.00	42.62	132.612	311.15
Ammonium Hydroxide	0.135	27	3.586	13.28
Sulfur	1.00	51.93	26.567	51.16
Zinc Oxide	0.750	58.73	19.891	33.869
ZDBC	0.300	51.73	7.944	15.357
TiO ₂	1.25	71.40	33.137	46.41
Wingstay L	0.501	51.18	13.278	25.943

The ammonium hydroxide was supplied by Mallinkrodt, St Louis, Missouri.

Approximately 2,574.4 grams of the compounded nitrile/neoprene latex blend were
 5 added to 474.9 grams of polyisoprene latex and 1480.0 grams of deionized water.

Glove samples were made according to the procedure described in Example 9.

These films were tensile tested as previously described, with the results described
 below in Table 7.

10 **Table 7**

	Thickness (in)	Tensile Strength (psi)	Elongation (%)	Modulus @ 100% Elongation (psi)	Modulus @300% Elongation (psi)	Modulus @400% Elongation (psi)	Modulus @500% Elongation (psi)	Modulus @600% Elongation (psi)
Sample 1	0.0049	2779	540	207	499	839	1826	466
Sample 2	0.0053	2633	546	197	475	793	1624	386
Sample 3	0.0053	2563	527	180	471	826	1889	--
Sample 4	0.0053	2431	519	193	485	860	1991	--
Mean	0.0052	2602	533	194	483	830	1833	0
SD	2E-4	145	12	11	12	28	154	0
Median	0.0053	2598	534	195	480	833	1857	0
Mean + 2.00 SD	0.0056	2891	557	216	508	887	2141	0
Mean - 2.00 SD	0.0048	2312	509	172	458	773	1524	0

Example 15. Preparation of 75 Parts Nitrile/5 Parts Neoprene/20 Parts**Polybutadiene Polymer Blend Film**

The nitrile/neoprene/polybutadiene blend latex was compounded as follows. Approximately 2,494 grams of nitrile latex were placed in a stainless steel tank and the following compounds were added in the amounts and sequence shown in Table 8.

Table 8

Compound	Parts	TSC %	Dry Wt. g	Wet Wt. g
Darvan WAQ	1.00	32.47	14.37	44.27
Neoprene 750	5.01	50.67	71.96	142.03
Polybutadiene	20.01	44.73	287.46	642.7
Ammonium Hydroxide	0.130	27.00	1.87	6.927
Sulfur	1.00	55.09	14.39	26.11
Zinc Oxide	0.757	62.61	10.88	17.381
ZDBC	0.301	52.47	4.318	8.230
TiO ₂	1.25	71.44	17.98	25.16
Wingstay L	0.504	52.41	7.248	13.83

The blend latex was allowed to stir overnight and the tank was capped. The polymer blend latex was then filtered into a 1 inch stainless steel dip tank. Films were made according to the dipping process as described in Example 9. The tensile properties of the polymer blend film were measured and the results are summarized in Table 9.

Table 9

	Thickness (in)	Tensile Strength (psi)	Elongati on (%)	Modulus @ 100% Elongatio n (psi)	Modulus @300% Elongatio n (psi)	Modulus @400% Elongatio n (psi)	Modulus @500% Elongatio n (psi)	Modulus @600% Elongatio n (psi)
Sample 1	0.0071	1538	560	200	461	680	1075	--
Sample 2	0.0071	1742	591	206	460	665	1015	787
Sample 3	0.0080	1312	543	195	445	655	1031	--
Sample 4	0.0071	1448	563	202	451	659	1016	--
Sample 5	0.0073	1870	568	212	484	733	1197	--
Sample 6	0.0073	1282	539	200	462	677	1042	--
Mean	0.0073	1532	561	202	461	678	1063	0
SD	3.49E-4	235	19	6	13	29	69	0
Median	0.0072	1493	562	201	461	671	1036	0
Mean + 2.00 SD	0.0080	2002	598	214	487	735	1201	0
Mean - 2.00 SD	0.0066	1062	523	191	434	621	924	0

While only a few embodiments of the invention have been described, those of ordinary skill in the art will recognize that the embodiment may be modified and altered without departing from the central spirit and scope of the invention. Thus, the embodiments described above are to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the following claims, rather than the foregoing description, and all changes that come within the means and ranges of equivalents of the claims are intended to be embraced.

CLAIMS

What is claimed is:

- 1 1. A glove comprising:
 - 2 (a) a blend of polymers comprising:
 - 3 (i) at least one butadiene based polymer; and
 - 4 (ii) at least one acrylonitrile copolymer;
- 5 wherein the blend is cured into an elastomeric film in the form of a glove.
- 1 2. The glove of claim 1, wherein butadiene based polymer is
 - 2 selected from the group consisting of poly(2-chloro-1,3-butadiene), poly(2-methyl-
 - 3 1,3-butadiene), polybutadiene, acrylonitrile-butadiene-styrene, its copolymers, and
 - 4 combinations thereof.
- 1 3. The glove of claim 1, wherein the acrylonitrile copolymer is
 - 2 an acrylonitrile-butadiene copolymer .
- 1 4. The glove of claim 1, wherein the acrylonitrile copolymer is a
 - 2 carboxylated acrylonitrile-butadiene copolymer.
- 1 5. The glove of claim 3, wherein the butadiene based polymer
 - 2 consists essentially of a copolymer of 2-chloro-1-3-butadiene and 2,3-dichloro-1,3
 - 3 butadiene.
- 1 6. The glove of claim 2, wherein the polymer blend consists
 - 2 essentially of a copolymer of 2-chloro-1,3-butadiene and carboxylated acrylonitrile-
 - 3 butadiene terpolymer, and poly(2-methyl-1,3-butadiene).
- 1 7. The glove of claim 2, wherein the polymer blend consists
 - 2 essentially of carboxylated acrylonitrile-butadiene terpolymer and poly(2-methyl-
 - 3 1,3-butadiene).

1 8. The glove of claim 1, wherein the butadiene based polymer
2 consists essentially of a combination of a copolymer of 2-chloro-1,3-butadiene and
3 poly(2-methyl-1,3-butadiene).

1 9. The glove of claim 5, wherein the polymer blend further
2 comprises natural rubber.

1 10. The glove of claim 1, wherein the butadiene based polymer
2 consists essentially of polybutadiene.

1 11. The glove of claim 1, wherein the butadiene based polymer
2 consists essentially of a combination of polybutadiene and a copolymer of 2-chloro-
3 1,3-butadiene and 2,3-dichloro-1,3-butadiene.

1 12. The glove of claim 1, wherein the polymer blend comprises 5
2 to 95 parts of one or more butadiene based polymer(s) by weight and 95 to 5 parts
3 acrylonitrile copolymer by weight, based on the total weight of the polymers.

1 13. The glove of claim 13, wherein the polymer blend comprises
2 75 to 50 parts one or more butadiene based polymer(s) by weight and 50 to 25 parts
3 acrylonitrile copolymer by weight, based on the total weight of the polymers.

1 14. The glove of claim 1, wherein the glove has a tensile strength
2 of at least about 1500 pound per square inch, a modulus at 500% of less than about
3 1500 pound per square inch and an elongation at break of at least about 500%.

1 15. The glove of claim 9, wherein the glove has a tensile strength
2 of at least about 1500 pound per square inch, a modulus at 500% of at least about
3 1500 pound per square inch and an elongation at break of at least about 500.

1 16. The glove of claim 10, wherein the glove has a tensile
2 strength of at least about 2150 pound per square inch, a modulus at 500% of at least
3 about 1050 pound per square inch and an elongation at break of at least about 550.

- 1 17. The glove of claim 1, further comprising chlorosulfinated
2 polyethylene rubber.
- 1 18. The glove of claim 1, wherein the polymer blend consists
2 essentially of carboxylated acrylonitrile-butadiene copolymer, a copolymer of 2-
3 chloro-1,3-butadiene and chlorosulfonated polyethylene.
- 1 19. An elastomeric article made of a polymer blend comprising:
2 (a) 5 parts to 95 parts by weight of at least one butadiene based
3 polymer; and
4 (b) 95 parts to 5 parts by weight at least one acrylonitrile
5 copolymer;
6 wherein the blend further comprises at least one crosslinking agent and at least one
7 vulcanization accelerator.
- 1 20. The elastomeric article of claim 19, wherein the butadiene
2 based polymer is selected from the group consisting of poly(2-chloro-1,3-
3 butadiene), poly(2-methyl-1,3-butadiene), polybutadiene, acrylonitrile-butadiene-
4 styrene terpolymer, styrene butadiene polymer, copolymers of the foregoing
5 butadiene based polymers, and combinations thereof.
- 1 21. The elastomeric article of claim 19, wherein the acrylonitrile
2 copolymer is an acrylonitrile-butadiene copolymer.
- 1 22. The elastomeric article of claim 21, wherein the acrylonitrile
2 copolymer is a carboxylated acrylonitrile-butadiene terpolymer.
- 1 23. The elastomeric article of claim 19, wherein the butadiene
2 based polymer consists essentially of copolymer of 2-chloro-1,3-butadiene and 2,3-
3 dichloro-1,3-butadiene.
- 1 24. The elastomeric article of claim 19, wherein the polymer
2 blend consists essentially of copolymer of 2-chloro-1,3-butadiene and 2,3-dichloro-
3 1,3-butadiene, acrylonitrile-butadiene copolymer and poly(2-methyl-1,3-butadiene).

1 25. The elastomeric article of claim 19, wherein the polymer
2 blend consists essentially of carboxylated acrylonitrile-butadiene terpolymer and
3 poly(2-methyl-1,3-butadiene).

1 26. The elastomeric article of claim 19, wherein the butadiene
2 based polymer consists essentially of a combination of copolymer of 2-chloro-1,3-
3 butadiene and 2,3-dichloro-1,3-butadiene and poly(2-methyl-1,3-butadiene).

1 27. The elastomeric article of claim 19, wherein the butadiene
2 based polymer consists essentially of polybutadiene.

1 28. The elastomeric article of claim 19, wherein the butadiene
2 based polymer consists essentially of a combination of polybutadiene and copolymer
3 of 2-chloro-1,3-butadiene- and 2,3-dichloro-1,3-butadiene.

1 29. The elastomeric article of claim 19, wherein the polymer
2 blend comprises 75 to 50 parts one or more butadiene based polymer(s) by weight
3 and 50 to 25 parts acrylonitrile copolymer by weight, based on the total weight of
4 the polymers.

1 30. The elastomeric article of claim 19, wherein the polymer
2 blend further comprises at least one crosslinking agent and at least one vulcanization
3 accelerator.

1 31. The elastomeric article of claim 19, wherein the polymer
2 blend is curable into an elastomeric film having a tensile strength of at least about
3 3650 pound per square inch, a modulus at 500% of at least 700 pound per square
4 inch and a elongation at break of at least about 700%.

1 32. The elastomeric article of claim 19, wherein the polymer
2 blend is curable into an elastomeric film having a tensile strength of at least about
3 1800 pound per square inch, a modulus at 500% of at least about 1050 pound per
4 square inch and an elongation at break of at least about 500%.

1 33. The elastomeric article of claim 19, wherein the polymer
2 blend is curable into an elastomeric film having a tensile strength of at least about
3 2150 pound per square, a modulus at 500% of at least about 1050 pound per square
4 inch and an elongation at break of at least about 550%.

1 34. A glove comprising an elastomeric blend of chloroprene
2 rubber and a carboxylated synthetic butadiene rubber.

1 35. A glove as claimed in claim 34, comprising an elastomeric
2 blend of chloroprene rubber and carboxylated nitrile butadiene rubber.

1 36. A polymer blend composition comprising:
2 (a) at least one chloroprene polymer; and
3 (ii) at least one acrylonitrile copolymer;
4 wherein the polymer blend further comprises at least one crosslinking
5 agent and at least one vulcanization accelerator.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08L 9/00

US CL : 525/232

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/232

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

none

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,187,232 A (MUSCH et al) 16 February 1993, see abstract.	1-36
Y	US 5,284,157 A (MILLER et al) 08 February 1994, see abstract.	1-36
Y	US 6,000,061 A (TANEJA et al) 14 December 1999, see abstract.	1-36

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T	Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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